

Conformational Effects upon the Stability and Reactivity of the [1.1]Ferrocenophan-1-yl and Diferrocenylmethyl Cations

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Rate and equilibrium constants have been measured for the interconversion of the [1.1]ferrocenophan-1-yl cation and [1.1]ferrocenophan-1-ol in $\text{H}_2\text{O}-\text{MeCN}$ (1 : 1 w/w) and compared with the corresponding values for interconversion of the diferrocenylmethyl cation and diferrocenylmethanol. The former cation is *ca.* 30 times more reactive towards addition of H_2O than is the non-cyclic analogue and is formed *ca.* 325 times faster by heterolysis of the alcohol at a given acid concentration.

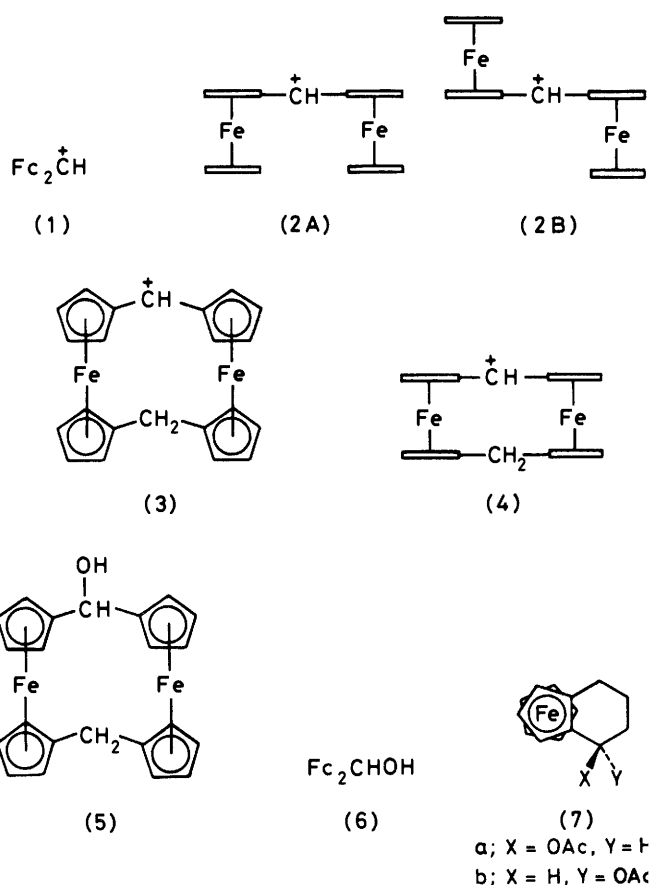
Rates of formation and reaction of ferrocenylalkyl cations are extremely sensitive to steric and conformational factors.¹ In the absence of overriding steric effects, heterolysis of substrates of the type FcCR_2X (Fc = ferrocenyl) occurs by preferential departure of the leaving-group (X^-) in the *exo*-direction with anchimeric assistance by the metal atom. For the reverse reaction, *exo*-addition of nucleophiles to ferrocenylalkyl cations is correspondingly favoured.² The situation is more complex with 1,1-diferrocenylalkyl systems such as the diferrocenylmethyl cation (1), which is conformationally mobile and may, in principle, react in a variety of conformations of which the *syn* (2A) and *anti* (2B) are extreme examples. In early papers,^{1a,c} we reported rate constants for formation of the cation (1) and nucleophilic additions to it. In order to explore further the relationship between conformation and reactivity, we made a similar study of the related [1.1]ferrocenophan-1-yl cation (3), which is constrained by the interannular CH_2 bridge to adopt a *syn*-conformation (4).

Results and Discussion

Methods for preparation of substrates and determination of rate and equilibrium constants are in the Experimental section. The results are in Table 1, which also includes corresponding data for the diferrocenylmethyl system.^{1a}

Comparison of k_f values shows that the bridged cation (3) is *ca.* 30 times more reactive towards addition of H_2O than is the non-cyclic cation (1). There is appreciable $\text{C} \cdots \text{O}$ bonding in the transition states for H_2O addition to ferrocenylalkyl ions, including (1),^{1c} but there is no reason to suppose that partial $sp^2 \rightarrow sp^3$ rehybridisation at the reaction centre would be less easy for cation (1) than for (3). It seems probable, therefore, that the higher reactivity of (3) is a consequence of its conformationally constrained structure,³ which allows unhindered *exo*-approach of a nucleophile to the reactive centre; see (4). The corresponding conformation (2A) of the diferrocenylmethyl cation is destabilised by repulsion between the pendant $\text{Fe}(\text{C}_5\text{H}_5)$ residues, and in other conformations such as (2B) approach of a nucleophile would be hindered by one or other of the Fc groups.

The ferrocenophanol (5) is *ca.* 325 times more reactive towards acid heterolysis than is diferrocenylmethanol (6) (see k_f values; Table 1). The electron-donating inductive effect of the additional CH_2 bridging group of the former may contribute to this reactivity difference, but only to a relatively minor extent; *e.g.* the rate constant for $\text{S}_{\text{N}}1$ hydrolysis of $\text{FcCH}(\text{OAc})\text{Me}$ is increased only *ca.* two-fold upon introduction of a 1'-methyl substituent.⁴ Furthermore, if electron-donating inductive effects were all-important, the bridged cation (3) should be less reactive than (1) towards



nucleophilic addition of H_2O , which is not the case. Rates of heterolysis of ferrocenylalkyl substrates are highly sensitive to the orientation of the leaving-group relative to the ferrocenyl residue; *e.g.*, the *exo*-acetate (7a) undergoes $\text{S}_{\text{N}}1$ hydrolysis at a rate *ca.* 2 500 times that of the *endo*-epimer (7b).⁵ Although neutral [1.1]ferrocenophanes are conformationally flexible,⁶ anchimeric assistance by *both* Fe atoms to departure of a water molecule can occur more effectively for acid heterolysis of the ferrocenophanol (5) than for diferrocenylmethanol (6), causing a higher reactivity for the former.

In summary, it appears that both the high reactivity of cation (3) towards H_2O addition and the fast acid heterolysis of alcohol (5), as compared with reactions of (1) and (6), are related to the conformations of (3) and (5), which permit unhindered *exo*-addition and departure of a water molecule.

Experimental

The BF_4^- salt of the cation (3) was prepared by reaction of [1.1]ferrocenophane⁷ with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in CH_2Cl_2 , and the alcohol (5) by reaction of this salt with aqueous NaOH , as described elsewhere.³ Acetonitrile (Mallinkrodt Spectrograde) was purified by double distillation from P_2O_5 and the fraction with b.p. 81.5°C was used.

Rate Measurements.—The rate of addition of H_2O to the cation (3) was measured by recording the disappearance with time of the cation absorbance at 755 nm following fast mixing of a solution (*ca.* 5 μl) of the BF_4^- salt in MeCN with *ca.* 3 ml of H_2O - MeCN (1 : 1 w/w) in a 1 cm cell at 25°C , using a Gilford spectrophotometer. Alcohol (5) was formed quantitatively. The rate of reaction ($t_{\frac{1}{2}} = \text{ca. } 0.9 \text{ s}$) is close to the limit of operation of the spectrophotometer but reproducible absorbance *versus* time curves were obtained over more than ten separate determinations. The first-order rate constant (k_t) was calculated in the usual way.^{1a}

The reverse reaction was followed at 25°C using a Durrum-Gibson stopped-flow spectrophotometer by mixing equal volumes of solutions of the alcohol (5) (10^{-4}M) and HCl (6×10^{-3} — $1.6 \times 10^{-2}\text{M}$) in H_2O - MeCN (1 : 1 w/w) and following the growth of absorbance of the cation (3) at 755 nm. All reactions went to completion. For each acid concentration (six were used), at least three separate rate determinations were carried out; reproducible absorbance *versus* time curves were obtained. The observed first-order rate constants ($k_{\psi} = k_t[\text{H}^+]$) were calculated as before and are in Table 2. A plot of k_{ψ} against $[\text{H}^+]$ was linear, passing through the origin, and the second-order rate constant was calculated from the slope.

Equilibrium Measurements.—Successive aliquots (1—3 μl) of 0.1M - HCl in H_2O - MeCN (1 : 1 w/w) were added to a solution (exactly 3 ml) of alcohol (5) (10^{-4}M) in H_2O - MeCN (1 : 1 w/w)

at 25°C in a 1 cm cell. Following each addition, the equilibrium concentrations of cation (3) and alcohol (5) in solution were obtained from the absorbance at 755 nm, at which wavelength the alcohol absorbance is negligible. For each solution, $[\text{H}^+]$ was calculated from the amount of HCl added, correcting for the amount consumed by reaction with the alcohol. The $\text{p}K_{\text{R}^+}$ value was calculated^{1a} from the relationship in equation (1). Similar values of $\text{p}K_{\text{R}^+}$ were obtained for different acid

$$\text{p}K_{\text{R}^+} = \log\{[\text{cation}]/[\text{alcohol}]\}_{\text{eq.}} - \log[\text{H}^+] \quad (1)$$

concentrations giving 20—90% conversion of alcohol into carbocation at equilibrium. The results are in Table 3. The same value of $\text{p}K_{\text{R}^+}$ was found when the determination was repeated using the carbocation absorbance at 375 nm, and a similar value was estimated from k_t/k_r .

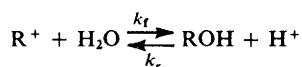
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Table 2. Rate constants for acid heterolysis of [1.1]ferrocenophan-1-ol^a

| $10^3[\text{HCl}]/\text{M}$ | k_{ψ}/s^{-1} | $k_{\psi}^{\text{av.}}/\text{s}^{-1}$ | $k_t/\text{l mol}^{-1} \text{s}^{-1}$ |
|-----------------------------|--------------------------|---------------------------------------|---------------------------------------|
| 3.0 | 37.6 | 38.7 | 1.29×10^4 |
| | 38.8 | | |
| | 39.8 | | |
| 4.0 | 47.0 | 47.6 | 1.19×10^4 |
| | 47.6 | | |
| | 48.3 | | |
| 5.0 | 60.5 | 60.8 | 1.22×10^4 |
| | 60.9 | | |
| | 61.0 | | |
| 6.0 | 69.8 | 71.8 | 1.20×10^4 |
| | 72.5 | | |
| | 73.1 | | |
| 7.0 | 82.6 | 85.2 | 1.22×10^4 |
| | 83.5 | | |
| | 89.6 | | |
| 8.0 | 92.4 | 96.6 | 1.21×10^4 |
| | 98.6 | | |
| | 98.7 | | |

Table 1. Rate and equilibrium constants^a

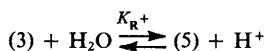


| R^+ | k_t/s^{-1} | $k_t/\text{l mol}^{-1} \text{s}^{-1}$ | $\text{p}K_{\text{R}^+}$ |
|------------------|-----------------------|---------------------------------------|--|
| (1) ^b | 2.66×10^{-2} | 37.2 | 3.15 ^c |
| (3) | 0.80 ^e | 1.22×10^4 ^f | 4.18 ^c 4.25 ^d |

^a At 25.0°C in H_2O - MeCN (1 : 1 w/w). ^b Values from ref. 1a. ^c Calculated from the rate constants. ^d Determined independently (see Experimental section). ^e $\pm 0.05 \text{ s}^{-1}$. ^f $\pm 0.07 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

^a In H_2O - MeCN (1 : 1 w/w) at 25.0°C ; a plot of k_{ψ} *versus* $[\text{HCl}]$ gives slope = $k_t = 1.22 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

Table 3. Determination of $\text{p}K_{\text{R}^+}$ value for the cation (3)^a



| 0.10M- HCl ^b (μl) | Molarity of $10^4[\text{HCl}]$ added | $\text{R}^+_{\text{eq.}}$ (%) | Molarity of $10^4[\text{H}^+]$ in solution ^c | $-\log[\text{H}^+]$ | $\log([\text{R}^+]/[\text{ROH}])_{\text{eq.}}$ | $\text{p}K_{\text{R}^+}$ ^d |
|---|--|-------------------------------|---|---------------------|--|---------------------------------------|
| 1 | 0.33 | 20.1 | 0.13 | 4.89 | -0.60 | 4.29 |
| 2 | 0.67 | 36.0 | 0.31 | 4.51 | -0.25 | 4.26 |
| 3 | 1.0 | 48.5 | 0.515 | 4.29 | -0.03 | 4.26 |
| 6 | 2.0 | 69.6 | 1.30 | 3.89 | 0.36 | 4.25 |
| 9 | 3.0 | 78.7 | 2.21 | 3.66 | 0.57 | 4.23 |
| 12 | 4.0 | 84.9 | 3.15 | 3.50 | 0.75 | 4.25 |
| 15 | 5.0 | 87.2 | 4.13 | 3.38 | 0.83 | 4.21 |

^a In H_2O - MeCN (1 : 1 w/w) at 25.0°C ; initial $[\text{alcohol}] = 10^{-4}\text{M}$. ^b Total volume added to a 3.0 ml solution of substrate. ^c $[\text{H}^+]$ in solution = $[\text{HCl}]$ added - $[(\% \text{R}^+)/100] \times 10^{-4}\text{M}$. ^d $\text{p}K_{\text{R}^+} = \log([\text{R}^+]/[\text{ROH}])_{\text{eq.}} - \log[\text{H}^+]$; average value = 4.25

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